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POSSIBILITIES OF HEAVY METALS AVAILABLE FOR PLANTS DETERMINATION IN THE SOIL OF AN INDUSTRIAL ZONE

MOŻLIWOŚCI OZNACZANIA METALI CIĘŻKICH DOSTĘPNYCH DLA ROŚLIN W GLEBACH TERENÓW PRZEMYSŁOWYCH

Abstract: For the determination of bioavailable form of heavy metals in soils the extraction methods using different extractors have been used in soil science. They presented analyzed content in the soil solution and different ways combined with the sorption complex. The problem is to indicate the boundary beyond which the element can be regarded as permanently absorbed. This problem is even larger in relation to soil under strong anthropopressure, which sorption complex is subjected to many actions dynamic sliding the boundary between sorption and desorption. The work shows the results of analyses made on the industrial soil material (Technosols), using as extractors 1 M salt solutions: KCl, MgCl₂, NH₄NO₃, KNO₃, NH₄OAc and 0.01 M CaCl₂, to demonstrate the potential bioavailability of Cd, Co, Cu, Ni, Pb and Zn. 1 M KNO₃ and KCl solutions were relatively stronger extractors of Ni, Cd and Co than the other ones. The relatively weak extractors of analysed heavy metals are 0.01 M CaCl₂, 1 M MgCl₂ and 1 M NH₄NO₃. An intermediate effect of 1 M NH₄OAc extraction has been marked.

Keywords: heavy metals extraction, available form of heavy metals, industrial soil

Introduction

The content of heavy metals in soils is showing a strong dependance from the form of land use and development direction of the state (impact of the pro-environmental or pro-industrial regulations). In the legal systems of most countries of the world [1, 2], and also in modern scientific considerations [3–6] a variation of heavy metals limits for protected nature areas, forests and parks, agricultural, urban, industrial and communications has been presented. Urban areas are often additionally divided on: residential areas, children playgrounds, parks, gardens, grounds services, manufacturing and others.

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The elements described in this study are presented in the environment as a micronutrients essential for living organisms (cobalt, copper, nickel, zinc), as well as elements of unknown physiological role (cadmium, lead) – [7]. Microelements occurring in soils in trace amounts are not environmental problem – on the contrary, the problem may be linked with their lack or limited bioavailability to plants. Otherwise this issue is presented within the industrial, urban, transport and the post-mining areas. Many authors have reported to them the problem of the oversized heavy metal content in the superficial layers of soils, directly threatening organisms, as well as indirectly – through the contamination of groundwaters, surface waters (the effect of infiltration and erosion) and air (the effect of the secondary secondary dust generation) – [8, 9].

If the case of necessity of the oversized heavy metals content determination exists, it appears the problem to indicate the state (form) of heavy metals in the given soil situation. The use of specific extractors, as well as their concentrations, operating conditions and time to reflect the existing and possible mobility of heavy metals in soil and aquatic environments is a commonly discussed problem [7, 10]. This is particularly important to form readily solved in water and poorly sorbed by the soil sorption complex (exchangeable form). Additional difficulty is the inconsistent behavior of mineral parts in soils of different mechanical composition, pH, salinity, organic matter content, redox potential and other characteristics [11, 12]. Widely discussed are differences in sorption and desorption phenomena in soils of urban and industrial areas showing the degradation and the presence of many different impurities – mainly of a waste origin [13–16].

The occurrence of various chemical and physical forms of the element in the analysed material is called speciation, and the identification and quantification is the subject of speciation analysis. The term is also used for naming of a variety analysis and extraction procedures. In the studies used for the speciation analysis of heavy metals in soils are used two basic types of proceedings [12]:

- single extraction - using a solution simulating the natural conditions of components transition from soil to water;

- sequential extraction - which consists of a raw of extraction procedures with solutions of increasing activity, aimed to capture different forms of components binding in the soil.

For the determination of bioavailable heavy metals form and assessment of migration ability of metals associated with the solid phase the single extraction in the analysis of soils, sewage sludge, as well as solid wastes is often used. The single extraction technique is implemented using different extractants: non-buffered salt solutions, such as MgCl₂, CaCl₂, NaNO₃, NH₄NO₃, buffered solutions as NH₄OAc/AcOH, as well as complexing compounds. In literature it can be found the information about a good reflection of this technique to the natural phenomena occurring under the influence of rainfall and floods of water [10, 17]. While, they are found different procedures for heavy metals determination in the bioavailable or potentially bioavailable forms (exchangeable / non-specifically sorbed fraction), different in respect of used extractor, its concentration, method and time of soil samples mixing with the extractor and the pH of extraction environment [10, 18].

Aim of this study is to compare the efficiency of Cd, Co, Cu, Ni, Pb and Zn extraction from soil samples of industrial soils (Technosols) using a single extraction technique with 1 M solutions of salts: KCl, MgCl₂, NH₄NO₃, KNO₃, NH₄OAc and 0.01 M solution of CaCl₂.

Research object description

Soil samples were taken from the area of metal industry located in Zielona Gora (western Poland), occupying an area of approximately 11.5 hectares. Industrial activities on this area began in 1876 on the construction of wooden wagons. Successively dealt with producing agricultural machinery, steel structures of industrial halls, bridges and railway stations. In 1886, the construction of railway freight wagons and passenger cars, tanks, mail wagons, refrigerated, etc. has been started During the Second World War the factory produced vehicles and equipment for the army. There have been produced armored trains, canon parts, military vehicles, submarine hulls, aircraft components. After 1945, the plant named Zastal, dealt with the production of rolling stock, freight cars, diesel locomotives and steel structures [19, 20]. At the beginning of the twenty-first century, on the described site is going production of rolling stock and steel structures.

Materials and methods

Soil samples preparation

According to IUSS WG WRB classification [21], the soils covering the area being under investigation represent a taxon: Urbic Transportic Toxic Technosols. Soil samples were taken as a aggregate ones, collected from the 0–20 cm layer. Each sample consisted of material mixed from the 30 individual sampling points. They have been marked as: Z1, Z2, Z3. Z1 and Z2 samples were taken from areas adjacent to production facilities, while the Z3 from internal parking hardened with slag and rubble. The soil samples were air dried (35 °C), after that passed through the 2-mm sieve.

Laboratory and statistical methods

All studies were conducted in summer, 2010. Mechanical composition was determined for the parts below 2 mm using areometric method. The $pH-H_2O$ and pH-1 M KCl values were measured with a glass electrode in the supernatant of a 1 : 2.5 soil : water suspension. EC was determined using conductometer EUTECH Instruments CyberScan in saturated paste. Basic sorption properties have been determined using the Kappen method for hydrolytic acidity (HA) and Pallmann method for bases content (BC). CEC was calculated by summarising the HA and BC. BS was calculated as a share of BC in the CEC and given in percent. Organic matter was determined by loss of ignition in a heating furnace at 550 °C.

For the analysis of heavy metals content from the aggregate sample was weighed 50 g of soil to each from the 18 plastic bottles; to every 3 bottles form this set 100 cm³ of extractor was added:

-1 M CH ₃ COONH ₄	exchangeable	form	acc.	to	[22],
– 1 M KCl	exchangeable	form	acc.	to	[23],
– 1 M KNO ₃	exchangeable	form	acc.	to	[23],
– 1 M MgCl ₂	exchangeable	form	acc.	to	[24],
– 0.01 M CaCl ₂	exchangeable	form	acc.	to	[25, 26],
– 1 M NH ₄ NO ₃	exchangeable	form	acc.	to	[25, 27].

For every combination the soil:solution ratio of 1:2 has been used. Bottles have been corked and placed in a rotating laboratory stirrer, leaving them for 1 hour of stirring at 25 °C [24]; stirrer speed: 60 times per minute. After that the suspension was filtered through medium paper filters to conical flasks, then poured into glass bottles. Markings have been made using a Varian atomic absorption spectrometer – FAAS method.

To ensure the accuracy and precision of the analysis, reagent blank and analytical duplicates were used. Three replicates have been used for each of the analytical procedures.

The results have been compared among themselves and also have been shown on the background of the subtotal content marked in aqua regia according to ISO 11466 [28].

The results were statistically analysed using Statsoft Statistica 9.1a for Windows procedures.

Results

Chosen physico-chemical characteristics of the soils

Samples from the industrial area were characterized by grain size of sand, which is typical for the area of Zielona Gora city. Admixtures of various waste materials and dust fallout from the lignite combustion have caused the effect of an alkaline pH and high total carbon content. Through the high water permeability of soils, the relatively low electrical conductivity has been recorded. Sorption properties are high due to about eight percent of the carbon content. From the data of Table 1 it is visible the uniform of basic physico-chemical properties of the described soils.

Table 1

Soil	Mechan of p	ical com parts < 2	position mm	TC	рН		EC	HA	BC	CEC	BS
sample	Sand [%]	Silt [%]	Clay [%]	[%]	in H ₂ O in 1 M KCl		$[\text{mS} \cdot \text{cm}^{-1}]$	$[\text{cmol}_{c} \cdot \text{kg}^{-1}]$			[%]
Z1	92	8	0	8.1	7.77	7.53	0.1178	1.35	43.10	56.60	76.14
Z2	94	6	0	8.1	8.04	7.87	0.1027	0.75	46.10	53.60	86.00
Z3	92	8	0	8.2	8.02	7.78	0.1056	0.82	43.90	52.15	84.18

Basic physico-chemical characteristics of the soils used in the experiment (mean values)

Heavy metals extraction

As a result of a single extraction of soil samples has been observed the low content of Cd, Co, Cu, Ni and Pb for 1 M NH₄NO₃ and 0.01 M CaCl₂. The lower results were obtained also with Zn extraction performed using 0.01 M CaCl₂. High content of Cd, Co, Cu, Ni and Pb were recorded when using for extraction 1 M KCl and 1 M KNO₃. For Zn, the highest content was noted in the 1 M NH₄OAc and 1 M MgCl₂ solutions. In the sample Z3 a relatively high content of Zn in the 1 M NH₄NO₃ extract has been also found.

Table 2

Soil	Extractant	Cd	Co	Cu	Ni	Pb	Zn		
sample	Extractant	$[mg \cdot kg^{-1}]$							
71	NH ₄ OAc	0.78 ± 0.02	6.43 ± 0.13	4.39 ± 0.36	1.56 ± 0.05	7.31 ± 0.17	137.6 ± 14.4		
	KC1	2.31 ± 0.04	31.38 ± 0.66	7.09 ± 0.47	10.57 ± 0.06	24.40 ± 0.67	27.0 ± 0.5		
	MgCl ₂	0.55 ± 0.02	1.12 ± 0.04	0.59 ± 0.03	1.22 ± 0.28	3.20 ± 0.33	34.9 ± 2.2		
	KNO3	2.09 ± 0.15	14.10 ± 0.53	7.79 ± 0.26	8.73 ± 0.68	18.71 ± 1.99	15.7 ± 3.6		
	NH ₄ NO ₃	0.19 ± 0.02	0.74 ± 0.01	0.28 ± 0.02	0.99 ± 0.01	0.65 ± 0.23	15.8 ± 0.2		
	CaCl ₂	0.22 ± 0.02	0.58 ± 0.05	not det.	0.37 ± 0.09	1.32 ± 0.63	10.4 ± 0.3		
	NH ₄ OAc	0.82 ± 0.02	7.30 ± 0.10	8.41 ± 0.21	2.13 ± 0.25	6.25 ± 0.31	197.7 ± 11.3		
	KC1	2.35 ± 0.15	30.47 ± 0.62	8.43 ± 0.21	9.35 ± 0.12	23.57 ± 1.32	29.3 ± 1.8		
70	MgCl ₂	0.47 ± 0.02	1.23 ± 0.06	1.27 ± 0.23	1.67 ± 0.14	2.55 ± 0.24	31.3 ± 1.0		
Z2	KNO3	2.85 ± 0.28	15.59 ± 0.21	10.18 ± 0.19	10.85 ± 3.24	22.47 ± 3.68	18.5 ± 1.9		
	NH ₄ NO ₃	0.27 ± 0.05	0.95 ± 0.05	1.07 ± 0.14	1.39 ± 0.16	1.52 ± 0.15	19.0 ± 0.5		
	CaCl ₂	0.33 ± 0.06	0.83 ± 0.04	0.13 ± 0.04	0.87 ± 0.02	0.81 ± 0.03	14.2 ± 1.1		
Z3	NH ₄ OAc	1.29 ± 0.01	7.95 ± 0.19	11.37 ± 0.62	7.05 ± 0.3	6.45 ± 0.57	396.5 ± 3.3		
	KC1	2.80 ± 0.03	25.60 ± 1.68	9.41 ± 0.12	12.73 ± 0.9	31.70 ± 0.88	37.5 ± 2.5		
	MgCl ₂	0.66 ± 0.05	1.60 ± 0.02	2.01 ± 0.24	1.66 ± 0.36	4.61 ± 0.48	239.4 ± 7.1		
	KNO3	3.51 ± 0.14	14.15 ± 1.07	10.32 ± 0.15	8.93 ± 1.36	21.15 ± 2.14	18.4 ± 3.2		
	NH ₄ NO ₃	0.26 ± 0.03	1.17 ± 0.05	3.51 ± 0.34	0.91 ± 0.08	4.55 ± 0.15	147.6 ± 14.9		
	CaCl ₂	0.26 ± 0.01	1.13 ± 0.05	0.09 ± 0.01	2.03 ± 0.05	2.45 ± 0.51	25.9 ± 4.0		

Results of heavy metals extraction from soils (mean content \pm std. dev.)

Designation the analyzed subtotal heavy metals form showed the presence of $[mg \cdot kg^{-1}]$:

Z1: Cd - 4.90, Co - 8.89, Cu - 58, Ni - 17.43, Pb - 146, Zn - 366;

Z2: Cd - 10.90, Co - 9.68, Cu - 115, Ni - 18.30, Pb - 128, Zn - 432;

Z3: Cd - 14.20, Co - 14.77, Cu - 366, Ni - 44.71, Pb - 714, Zn - 2713.

Referring the data obtained from the analysis of heavy metals content in the extracts described in Table 1 to the subtotal content (Table 3), it must be noted relatively high efficiency of 1 M KCl and 1 M KNO₃ to the extraction of Cd, Ni and Pb. 1 M KCl was also an effective extractor of Co. For this metal 1 M KNO₃ has been less effective extractor than 1 M NH₄OAc. With respect to Cu, 1 M KCl, 1 M KNO₃, as well as 1 M NH₄OAc proved to be more effective extractors than other ones. However, there was

internal divergence between these three solutions compared to each of the analyzed samples. In the case of zinc the highest effectiveness of 1 M NH_4OAc has been evidently proved.

Table 3

Soil	Extractant	Cd	Со	Cu	Ni	Pb	Zn	
sample		[%]						
	NH ₄ OAc	15.9	72.3	7.6	9.0	5.0	37.6	
	KCl	47.1	35.3	12.2	60.6	16.7	7.4	
71	MgCl ₂	11.2	12.6	1.0	7.0	2.2	9.5	
	KNO3	42.7	15.9	13.4	50.1	12.8	4.3	
	NH ₄ NO ₃	3.9	8.3	0.5	5.7	0.4	4.3	
	CaCl ₂	4.5	6.5	0.0	2.1	0.9	2.8	
	NH ₄ OAc	7.5	75.4	7.3	11.6	4.9	45.8	
	KC1	21.6	31.5	7.3	51.1	18.4	6.8	
70	MgCl ₂	4.3	12.7	1.1	9.1	2.0	7.2	
22	KNO3	26.1	16.5	8.9	59.3	17.6	4.3	
	$\rm NH_4NO_3$	2.5	9.8	0.9	7.6	1.2	4.4	
	CaCl ₂	3.0	8.6	0.1	4.8	0.6	3.3	
Z3	NH ₄ OAc	9.1	53.8	3.1	15.8	0.9	14.6	
	KC1	19.7	17.3	2.6	28.5	4.4	1.4	
	MgCl ₂	4.6	10.8	0.5	3.7	0.6	8.8	
	KNO3	24.7	9.5	2.8	20.0	3.0	0.7	
	NH ₄ NO ₃	1.8	7.9	1.0	2.0	0.6	5.4	
	CaCl ₂	1.8	7.7	0.0	4.5	0.3	1.0	

Extraction efficiency of analysed chemical solutions compared to the subtotal content

For each extractor can be determined the effectiveness array:

1 M NH ₄ OAc	Co > Zn >	Ni > Cd >	Cu > Pb;
1 M KCl	Ni > Cd >	Co > Pb >	Cu > Zn;
1 M MgCl ₂	Co > Zn >	Cd > Ni >	Pb > Cu;
1 M KNO ₃	Ni > Cd >	Co > Pb >	Cu > Zn;
1 M NH ₄ NO ₃	Co > Ni >	Zn > Cd >	Cu = Pb;
0.01 M CaCl ₂	Co > Ni >	Cd > Zn >	Pb > Cu.
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It can be indicated a number of similarities in setting of the analysed heavy metals extraction effectiveness arrays for the pairs of solutions: 1 M KCl and 1 M KNO₃, 1 M NH_4OAc and 1 M MgCl₂, 1 M NH_4NO_3 and 0.01 M CaCl₂.

Discussion

The difficulty of determining the bioavailable form of heavy metals in soils consists of diverse physiological responses of plants to the content of these elements. as well as the dynamics of changes in the sorption complex of soil and soil solution. Therefore, in many cases the authors do not use the pure concept of bioavailability, but potential bioavailability of elements. This means that under certain environmental conditions (eg acidification. shifting the balance between the processes of oxidation and reduction) part of the metals sorbed in the soil sorption complex can be desorbed and found in the soil solution. We come here to some element of risk analysis – how often can such conditions happens and on what scale? In the environmental analysis is often thought, that even the probability of one occurrence of such circumstances is enough for suggesting potential availability of elements.

Basta et al [29] and Rao et al [10] are suggesting caution in estimating the uptake of heavy metals by plants determined in soils using single extraction. This is due to the complex physiological conditions. This indicates a better procedure involving the use of the term of the potential availability of heavy metals for organisms. This problem does not resolve to adopt a different technique for determining the elements described in the soils. Sequential extraction method is fraught with the same dilemma.

The use of different extractors to perform into the liquid phase salts of heavy metals contained in the soil gives a different effect on the results of their content. Hence the need for a detailed description of not only the form of metal in the soil. but also the methodology of its extraction. Rao et al [10] are showing a huge variety of procedures available for the determination of bioavailable form of heavy metals in soils.

0.01 M CaCl₂ is extractant recommended in the Netherlands for heavy metals available for plants form evaluation [30]. Menzies et al [17] pointed out this extractor as well reflecting the phytoavailability of Cd. Ni and Zn. In light of the reported research in this paper should be noted. that this solution has demonstrated the effectiveness of some 7 % of subtotal Co content and about 3 % of subtotal Cd. Ni and Zn content. In other cases, the values were extremely low. Low scores of Cu extraction using calcium chloride solution (≤ 0.4 %) have been described by Schramel et al [25]. Sahuquillo et al [31] have found that for the most of heavy metals 0.01 M CaCl₂ extract no more than 1 % of their total form, but for Cd and Zn can be noted higher results (even up to 40 % Cd and 12 % Zn). The presented study did not support this thesis.

1 M MgCl₂ solution, proposed by Navas and Lindhorfer [32]. proved in the research effectiveness to Cd, C, Ni and Zn extraction. Significantly lower scores have been noted for Cu and Pb.

1 M NH₄NO₃ is a standard extractant for the described in the paper heavy metal form in Germany [33]. The studies have shown the ability to release more than 5 % of the subtotal Co and Ni form wits content determination. this solution. For other metals the extraction potential of described solution was low. Low scores of Cu extraction using calcium chloride solution (≤ 0.4 %) have been described by Schramel et al [25].

1 M KNO₃ can be used for non-specific sorbed (exchangeable) heavy metals content determination [18].

 NH_4OAc is a salt of a weak base. According to Schramel et al [25] this compound formed metal acetate complexes. what tends to prevent readsorption of released cations. Menzies et al have pointed out NH4OAc as well reflecting phytoavailability of Cd [17]. In view of the presented work this extractor has mobilised 7.5–15.9 % of subtotal Cd. which indeed seems to confirm this thesis. Generally, described extractor can be characterised as balanced one in terms of extraction force for the analyzed elements. except cobalt. Using of 1 M NH₄OAc for Co extraction may indicate excessively high mobility of this metal.

1 M KCl solution has been described by Grove et al [23] as similar in action with 1 M NH_4OAc . As has been shown for the situation described in this paper. the only similarity between 1 M KCl and NH_4OAc can be identified in the extraction of Cu. Other heavy metals were extracted with different intensity. although in both cases with high effectiveness in compare to the other analysed solutions.

According to Szumska and Gworek [18]. using the chloride salt as heavy metal extractors gives higher scores than in the case of nitrate salts use by the same cation and solution concentration. The examined relationship 1 M KNO₃ to 1 M KCl confirm this thesis in case of Co (mean 28.1 % vs. 14.0 % of subtotal form). Ni (mean 46.7 % vs. 43.1 %). Pb (mean 13.2 % vs. 11.1 %) and Zn (mean 5.2 % vs. 3.1 %). With respect to Cd and Cu the solutions of described salts behave similarly in terms of extraction efficiency – respectively (average values): 29.5 % vs. 31.2 % and 7.4 % vs. 8.4 %.

Conclusions

Many authors suggest the need for sequential extraction use. as giving more detailed information on the metal bind form in soil. They describe the single extraction method as not enough selective. It is difficult do not agree with these opinions. however. noting that the phenomena occurring in nature are generally less selective. For the practice turns out to be important to estimate the size of the possible release of metal into the soil solution under different external conditions and different properties of soils. Different extractors make it possible to desorbe of various amounts of metallic ions. KNO₃ and KCl are relatively stronger extractors of Ni. Cd and Co in relation to the other extractors. Relatively weak extractors of the analyzed heavy metals are: $CaCl_2$, MgCl₂ and NH₄NO₃. An intermediate effect of 1 M NH₄OAc extraction has been marked.

It should be remembered that this does not mean negation or preference of the definite extractors – they reflect some special conditions that may occur in nature. From this reason, they can be appropriate for different applications.

It is not possible to identify one from the analysed set as a universal extractor for estimating available for plants form of all heavy metals.

For different soil conditions and external conditions of extraction can be indicated different preferences for use of specific extractor to estimate the content of bioavailable form of heavy metals.

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MOŻLIWOŚCI OZNACZANIA METALI CIĘŻKICH DOSTĘPNYCH DLA ROŚLIN W GLEBACH TERENÓW PRZEMYSŁOWYCH

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Abstract: Do oznaczenia formy biodostępnej metali ciężkich w glebach używane są w gleboznawstwie metodyki oparte o ekstrakcję z użyciem różnych ekstraktorów. Ukazują one analizowaną zawartość w roztworze glebowym oraz w różny sposób związaną z kompleksem sorpcyjnym gleb. Problemem jest wskazanie granicy, poza którą dany pierwiastek można uznać za zabsorbowany trwale. Problem ten jest jeszcze wiekszy w odniesieniu do gleb pod silną antropopresją, których kompleks sorpcyjny podlega wielu działaniom dynamicznie przesuwającym granicę sorpcji i desorpcji. W pracy ukazano wyniki działania na glebę industrialną (Technosols) 1 M roztworami soli: KCl, MgCl₂, NH₄NO₃, KNO₃ i NH₄OAc oraz 0.01 M CaCl₂, celem wykazania potencjalnej biodostępności Cd, Co, Cu, Ni, Pb i Zn. 1 M roztwory KNO₃ i KCl okazały się relatywnie mocniejszymi ekstraktorami Ni, Cd i Co niż pozostałe. Relatywnie słabymi ekstraktorami wobec analizowanych metali ciężkich są 0.01 M CaCl₂, 1 M MgCl₂ oraz 1 M NH₄OA₃. Pośrednią mocą odznaczył się 1 M NH₄OAc.

Słowa kluczowe: ekstrakcja metali ciężkich, biodostępne formy metali ciężkich, strefy przemysłowe